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各PCTガゼットの巻頭に掲載されている「コードと略語
のガイドスノート」を参照。

(54) Title: PROCESS FOR PRODUCTION OF FLUORINE-CONTAINING NORBORNENE DERIVATIVES

(54) 発明の名称: 含フッ素ノルボルネン誘導体の製造法

(57) Abstract: Novel norbornene derivatives bearing fluorinated ketone or fluorinated alcohol moieties attached directly to norbornene skeleton, which are useful as material of chemically amplified photoresists for F₂ laser lithography having excellent transparency and improved dry etching resistance; fluorine-containing polymers produced by using the derivatives as comonomer; and chemically amplified photoresist compositions each comprising a fluorine-containing polymer described above, a photoacid generator, and a solvent.

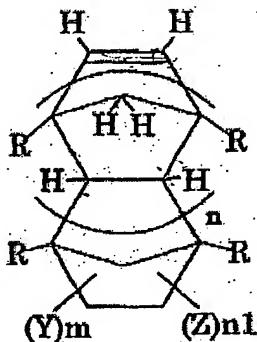
(57) 要約:

透明性に優れ、かつ耐ドライエッティング性が改善されており、F₂レー
ザー用の化学增幅型フォトレジスト用の材料であって、ノルボルネン骨格
に直接含フッ素ケトン部位または含フッ素第3級アルコール部位が結合し
た新規ノルボルネン誘導体、それを共重合モノマーとして得られる含フッ
素重合体、該含フッ素重合体と光酸発生剤と溶剤とからなる化学增幅型フ
オトレジスト組成物を提供する。

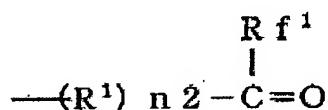
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Claims of the Patent

1. Method of making the fluorine-containing norbornene derivative that has a ketone-containing structure and is expressed by the formula (2):

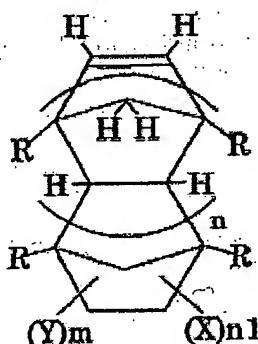


[In the formula, Z's are same or different and all of them are

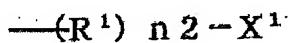


(in the formula Rf^1 , R^1 , n_2 are same as described below); Y, R, n, m, n1 are same as described below],

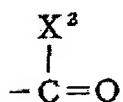
the method being characterized by reacting the norbornene derivative that is expressed by the formula (1):



[In the formula, X's are same or different, and all of them are

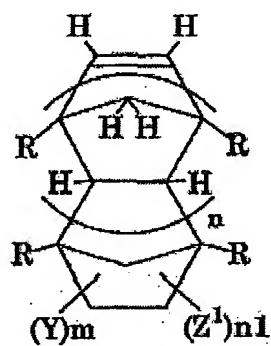


(in the formula, X^1 is $-\text{COOR}^2$ or

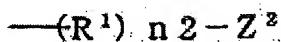


(R² is an alkyl group of 1 ~ 5 carbons, X² is a halogen atom); R¹ is a divalent organic groupd, n2 is 0 or 1); Y's are same or different and it is H, F, Cl, an alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group that may contain the ether bond of 1 ~ 10 carbons; R's are same or different and it is an H or an alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here, m + n1 = 6] and the fluoro alkylation agent that introduces Rf¹ (Rf¹ is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond) into the X in the formula (1).

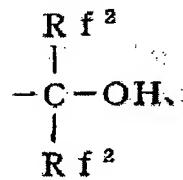
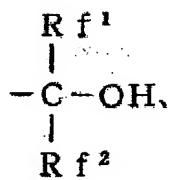
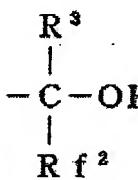
2. Method of making the fluorine-containing norbornene derivative that has the structure of fluorine- containing tertiary alcohol structure and is expressed by the formula (4):



[In the formula, Z¹'s are same or different and they are



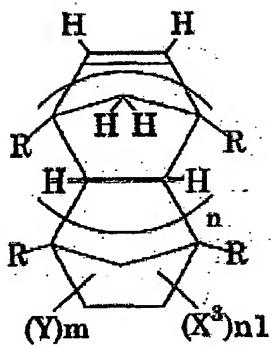
(in the formula, Z3 is



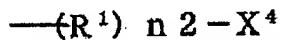
or

(in the formula, Rf², Rf¹ and R³ are same as described below); R1 is a divalent organic group; n2 is 0 or 1; Y, R, n, m and n1 are same as described below]

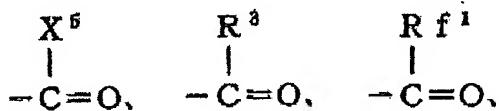
the method being characterized by reacting the fluorine-containing norbornene derivative that is expressed by the formula (3):



[In the formula, X^3 , s are same or different and they are

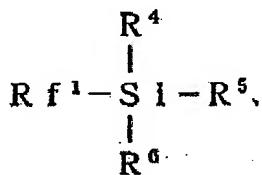


(in the formula, X^4 is $-COOR^2$ group or



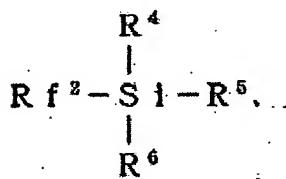
(in the formula, R^2 is an alkyl group of 1 ~ 5 carbons; X^5 is a halogen atom; R^3 is H or a hydrocarbon group of 1 ~ 10 carbons; Rf^1 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having ether bond); R^1 is a divalent organic group; $n2$ is 0 or 1); Y's are same or different and it is an H, F, Cl, alkyl group of 1 ~ 10 carbons, a fluorine-containing alkyl group that may contain the ether bond of 1 ~ 10 carbons; R's are same or different and it is H or an alky group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here, $m + n1 = 6$] and the fluoro alkylation agent that introduces Rf^2 (Rf^2 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having ether bond) into the X^4 .

3. The method of making described in Claim 1 in which the fluoro alkylation agent is the fluoro silane compound that is expressed by



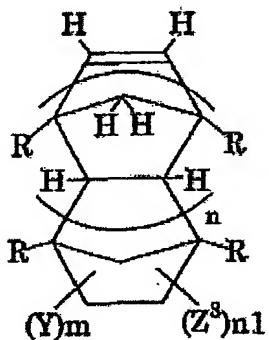
(in the formula, Rf^1 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; R^4 , R^5 , R^6 are same of different and they are hydrocarbon group of 1 ~ 10 carbons).

4. The method of making described in Claim 2 in which the fluoro alkylation agent is the fluoro silane compound that is expressed by

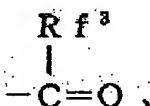


(in the formula, Rf^2 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; R^4 , R^5 , R^6 are same or different and they are hydrocarbon group of 1 ~ 10 carbons).

5. The norbornene derivative that has the ketone-containing structure and is expressed by the formula (5):

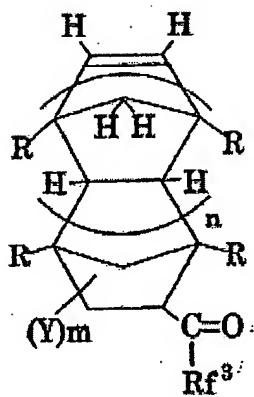


[In the formula, Z^3 's are same or different and they are

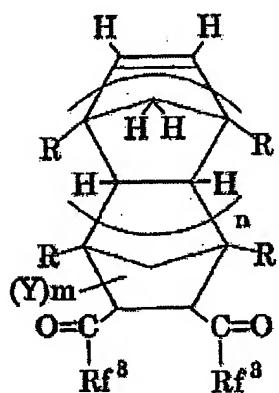


(in the formula, Rf^3 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; Y's are same or different and it is H, F, Cl, alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group that may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here, $m + n1 = 6$].

6. Norbornene derivative hat has the fluorine-containing ketone structure and is expressed by the formula (6):



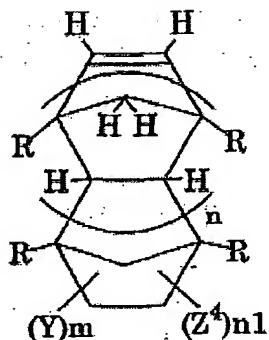
(In the formula, Rf^3 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; Y's are same or different and it is H, F, Cl, alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group that may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is 5) or by the formula (7):



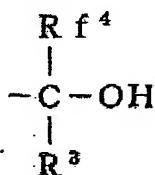
(In the formula, Rf^3 is a fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; Y's are same or different and it is H, F, Cl, alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group of 1 ~ 10 carbons that may contain ether bond; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is 4).

7. Norbornene derivative having the fluorine-containing ketone structure described in Claim 5 or 6 in which the Rf^3 in the formulas (5), (6), (7) is CF_3 .

8. Norbornene derivative that has the fluorine-containing alcohol structure and is expressed by the formula (8):

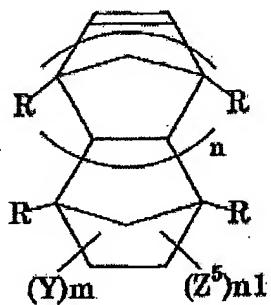


[In the formula, Z^4 's are same or different and all of them are

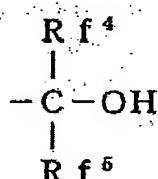


(in the formula, Rf^4 's are same or different and they are fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; R^3 is H or hydrocarbon group of 1 ~ 10 carbons; Y's are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group which may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here $m + n1 = 6$].

✓ 9. Norbornene derivative that has the fluorine-containing alcohol structure and is expressed by the formula (9):



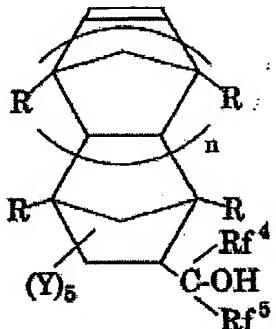
[In the formula, Z^5 's are same or different and all of them are



(in the formula, Rf^4 , Rf^5 are same or different and they are fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; Y's

are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group which may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here m + n1 = 6].

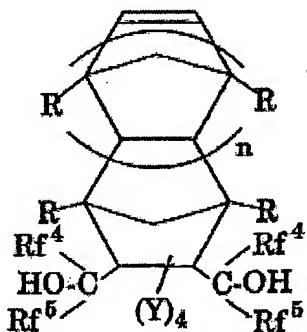
10. Norbornene derivative that has the fluorine- containing alcohol structure and is expressed by the formula (10):



(in the formula, Rf⁴, Rf⁵ are same or different and they are fluorine- containing alkyl group of 1 ~ 10 carbons or a fluorine- containing alkyl group having the ether bond; Y's are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group which may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5).

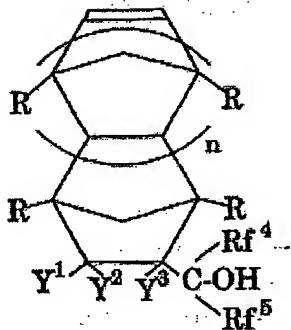
11. Norbornene derivative that has the fluorine- containing alcohol structure described in Claim 9 or 10 in which at least one of the substitution group Y in the formulas (9) or (10) is a fluorine-, containing alkyl group that may contain F or ether bond of 1 ~ 10 carbons.

12. Norbornene derivative that has the fluorine- containing alcohol structure and is expressed by the formula (11):



(in the formula, Rf⁴, Rf⁵ are same or different and they are fluorine- containing alkyl group of 1 ~ 10 carbons or a fluorine- containing alkyl group having the ether bond; Y's are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group which may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5).

13. Norbornene derivative that has the fluorine- containing alcohol structure and is expressed by the formula (12):



(in the formula, Rf⁴, Rf⁵ are same or different and they are fluorine-containing alkyl group of 1 ~ 10 carbons or a fluorine-containing alkyl group having the ether bond; Y¹, Y², Y³ are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group which may contain ether bond of 1 ~ 10 carbons; R's are same or different and it is H or alkyl group of 1 ~ 10 carbons; n is an integer of 0 ~ 5. Here, at least one of Y¹, Y², Y³ is F or an fluorine-containing alkyl group that may contain the ether bond of 1 ~ 10 carbons).

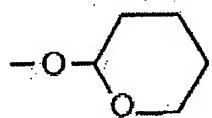
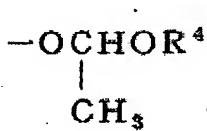
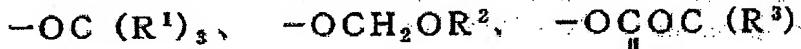
14. Norbornene derivative that has the fluorine-containing alcohol structure described in Claim 13 in which Y¹ and Y² are H and Y³ is F or CF₃.

15. Norbornene derivative that has the fluorine-containing alcohol structure described in Claim 13 in which Y¹ and Y² are F and Y³ is F or CF₃.

16. Norbornene derivative that has the fluorine-containing alcohol structure described in any one of Claims 8 ~ 15 in which Rf⁴ and Rf⁵ are CF₃.

17. The norbornene derivative that has the fluorine-containing alcohol structure described in any one of Claims 8 ~ 16, the said norbornene derivative having the protective acid reactive functional group -OQ¹ that protects the hydroxyl group.

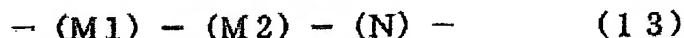
18. The norbornene derivative described in Claim 17 in which the protective acid reactive functional group -OQ¹ is at least the one that is selected from the group consisting of



(in the formulas, R¹, R², R³ and R⁴ are alkyl group of 1 ~ 5 carbons).

19. The fluorine-containing polymer of number average molecular weight of 500 ~ 1000,000 containing 1 ~ 99 mol % of structural unit M1, 1 ~ 99 mol % of structural unit M2 and 0 ~ 98 mol % of structural unit N, the fluorine-containing polymer being a

polymer that has a cyclic structure in the polymer main chain that is expressed by the formula (13):



(in the formula, M1 is the structural unit that originates from at least one type that is selected from the fluorine-containing norbornene derivative described in any one of Claims 5 ~ 18; M2 is an ethylene monomer of 2 or 3 carbons which is the structural unit obtained from the fluorine-containing monomer that contains at least one fluorine atom; N is a structural unit that originates from a monomer that can copolymerize with M1, M2).

20. Fluorine-containing polymer described in Claim 19 in which M1/ M2 is in a mol % ratio of 30/70 ~ 70/30 when $(\text{M1}) + (\text{M2}) = 100 \text{ mol \%}$ in the formula (13).

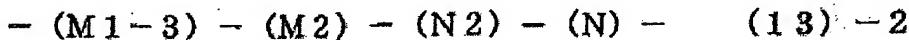
21. The fluorine-containing polymer of number average molecular weight of 500 ~ 1000,000 containing 1 ~ 98 mol % of structural unit M1-1, 1 ~ 98 mol % of structural unit M1-2 and 0 ~ 97 mol % of structural unit N, the fluorine-containing polymer being a polymer that has a cyclic structure in the polymer main chain that is expressed by the formula (13)-1:



(in the formula, M1-1 is the structural unit that originates from at least one type that is selected from the norbornene derivative having the fluorine-containing alcohol structure described in any one of Claims 8 ~ 16; M1-2 is the structural unit that originates from at least one type selected from the norbornene derivative having the protective acid reactive functional group described in Claim 17 or 18; M2 and N are the polymers having the cyclic structure in the polymer main chain that is expressed by the formula (13)). When $(\text{M1-1}) + (\text{M1-2}) + \text{M2} = 100 \text{ mol \%}$, $\{(\text{M1-1}) + (\text{M1-2})\}/\text{M2}$ is in the ratio of 30/70 ~ 70/30 mol %.

22. Fluorine-containing polymer described in Claim 21 in which, when $(\text{M1-1}) + (\text{M1-2}) = 100 \text{ mol \%}$, $(\text{M1-1})/(\text{M1-2})$ is in the ratio of 90/10 ~ 50/50 mol %.

23. Fluorine-containing polymer that is expressed by the formula (13)-2:



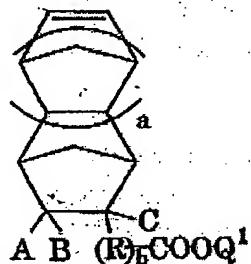
(in the formula, the structural unit M2 is same as the formula (13); structural unit M1-3 is what originates from at least one type selected from the norbornene derivative described in any one of Claims 8 ~ 18; structural unit N2 consists of the cyclic aliphatic unsaturated hydrocarbon that can copolymerize with the monomer that constitutes M2 and N and, further, it originates from the cyclic aliphatic unsaturated hydrocarbon that has the

COOH group or the acid- dissociating functional group which can be converted to carboxyl group by acid;

structural unit N originates from the monomer that can copolymerize with the monomers that constitute the structural units M1-3, M2 and N2). When $(M1-3) + M2 + N2 = 100$ mol %, $\{(M1-3) + M2\} / M2$ is in the mol % ratio of 70/30 ~ 30/70. The structural unit M1-3 is 1 ~ 98 mol %, the structural unit M2 is 1 ~ 98 mol %, structural unit N2 is 1 ~ 98 mol %, structural unit N is 0 ~ 97 mol %.

24. The fluorine- containing polymer described in Claim 23 in which the structural unit N2 in the fluorine- containing polymer of the formula (13) – 2 is the structural unit that originates from the norbornene derivative having COOH group or the acid- dissociating functional group that can be converted to carboxyl group by acid.

25. The fluorine- containing polymer described in Claim 24 in which the norbornene derivative having COOH group or the acid- dissociating functional group that can be converted to carboxyl group by acid is the one that is expressed by the formula:



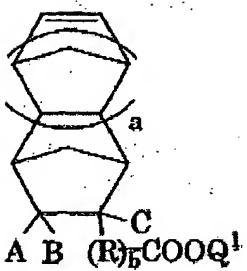
(in the formula, A, B and C are H, F, alkyl group of 1 ~ 10 carbons or fluorine- containing alkyl group of 1 ~ 10 carbons; R is a divalent hydrocarbon group of 1 ~ 20 carbons, fluorine- containing alkylene group of 1 ~ 20 carbons, or fluorine- containing alkylene group having the ether bond of 2 ~ 100 carbons; a is an integer of 0 or 1 ~ 3; b is 0 or 1; COOQ¹ is COOH group or the acid- dissociating functional group that can be converted to carboxyl group by acid; here, when b is 0 or R does not contain fluorine atom, any one of A ~ C is a fluorine atom or fluorine- containing alkyl group).

26. Fluorine- containing polymer that is expressed by the formula (13) – 3:

$$- (M1-1) - (M2) - (N2-1) - (N) - \dots (13) - 3$$

(in the formula, the structural unit M1-1, M2 are same as the formula (13) – 1 described in Claim 21;

structural unit N2-1 is what originates from the norbornene derivative which is expressed by the formula (3) – 1;



(in the formula, COOQ^1 is the acid-dissociating functional group that can be converted to carboxyl group by acid and A, B, C, R, a and b are same as described before);

structural unit N is what originated from the monomer that can copolymerize with the monomers which constitute the structural units M1-1, M2 and N2-1);

when $(\text{M1-1}) + (\text{M2}) + (\text{N2-1}) = 100 \text{ mol \%}$, $\{(\text{M1-1}) + (\text{N2-1})\} / (\text{M2})$ is in the mol % ratio of 70/30 ~ 30/70; also, when $(\text{M1-1}) + (\text{N2-1}) = 100 \text{ mol \%}$, $(\text{M1-1}) / (\text{N2-1})$ is in the mol % ratio of 95/5 ~ 50/50; structural unit M1-1 is contained by 1 ~ 98 mol %, structural unit M2 by 1 ~ 98 mol %, structural unit N2-1 by 1 ~ 98 mol %, structural unit N by 0 ~ 97 mol %.

27. Fluorine-containing polymer described in any one of Claims 19 ~ 26 in which the structural unit M2 is at least one type of monomer selected from the group consisting of tetra fluoro ethylene, chloro trifluoro ethylene, vinylidene fluoride and vinyl fluoride.

28. Fluorine-containing polymer described in any one of Claim 27 in which the structural unit M2 is the structural unit obtained from tetra fluoro ethylene or chloro trifluoro ethylene.

29. Chemically amplified photo resist composition which is a composition consisting of

- (A) The fluorine-containing polymer having the OH group and/or the group in which the hydroxyl group is protected by the protective acid reactive functional group $-\text{OQ}^1$;
- (B) Photo acid generating agent;
- (C) Solvent;

the fluorine-containing polymer (A) that has the acid reactive group being the fluorine-containing polymer that is expressed by the formula (14):



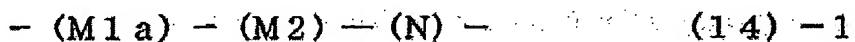
(in the formula, M1a is the structural unit originating from the norbornene derivative that has the fluorine-containing alcohol structure of the previously described formulas (8) ~ (12) and/or the compound in which the hydroxyl group of the norbornene derivative that has the structure of fluorine-containing alcohol of the previously described formulas (8) ~ (12) is protected by the protective acid reactive functional group $-\text{OQ}^1$; M2 is the

structural unit which is an ethylene monomer of 2 or 3 carbons and is obtained from the fluorine-containing monomer that contains at least one fluorine atom; N is a structural unit that originates from the monomer which can copolymerize with the structural units M1a, M2).

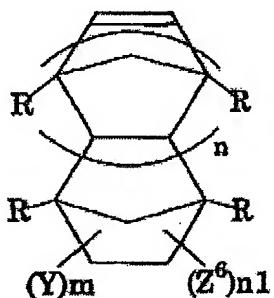
30. Chemically amplified photo resist composition described in Claim 29 which is a fluorine-containing polymer and is a composition consisting of

- (A) The fluorine-containing polymer having the OH group or the group that can be altered to OH group by dissociation with an acid;
- (B) Photo acid generating agent and
- (C) Solvent;

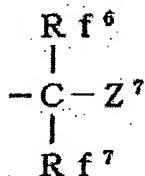
The said fluorine-containing polymer (A) is expressed by the formula (14)-1:



(in the formula, the structural unit M1a is expressed by the formula (15)



(in the formula, Z⁶'s are same or different and is



(Rf⁶, Rf⁷ are same or different and they are fluorine-containing alkyl group of 1 ~ 10 carbons or fluorine-containing alkyl group having ether bond; Z⁷ is OH group or a group that changes to OH group by dissociation by reacting with acid); Y's are same or different and they are H, F, Cl, alkyl group of 1 ~ 10 carbons, or the fluorine-containing alkyl group which may contain the ether bond of 1 ~ 10 carbons; R's are same or different and they are H or alkyl group of 1 ~ 10 carbons; n is 0 or an integer of 1 ~ 5; m is an integer of 1 ~ 5; n1 is an integer of 1 ~ 5; here, m + n1 = 6)

and is a structural unit originating from at least one selected from the norbornene derivative having the fluorine-containing alcohol structure expressed by this;

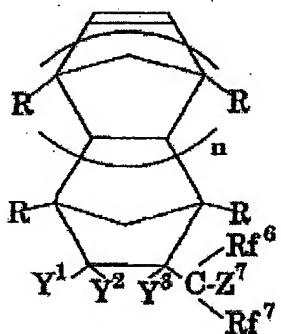
the structural unit M2 is what originates from the monomer that is an ethylene monomer of 2 or 3 carbons and has at least one fluorine atom;

the structural unit N is what originates from the monomer that can copolymerize with the structural units M1 and M2);

when $M1a + M2 = 100 \text{ mol \%}$, $M1a/M2$ has a mol % ratio of $1/99 \sim 70/30$ and the structural unit M1a is contained by $1 \sim 99 \text{ mol \%}$, structural unit M2 by $1 \sim 99 \text{ mol \%}$, structural unit N by $0 \sim 98 \text{ mol \%}$ and number average molecular weight is $500 \sim 1000,000$.

31. Chemically amplified photo resist composition described in Claim 30 where, in the structural unit M1a of the previously described fluorine-containing polymer (A), at least one of the substitution group Y described in the formula (15) is F or a fluorine-containing alkyl group that may contain the ether bond of $1 \sim 10$ carbons.

32. Chemically amplified photo resist composition described in Claim 30 which is characterized by that, in the previously described fluorine-containing polymer (A), the structural unit M1a is what originated from the fluorine-containing norbornene derivative that is expressed by the formula (16):



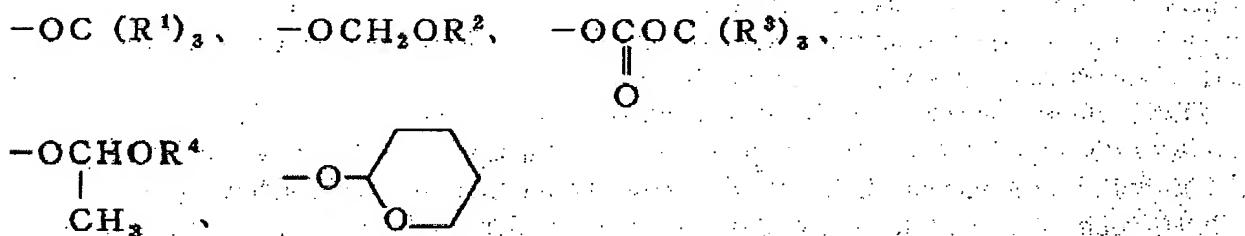
(Rf⁶, Rf⁷ are same or different and they are fluorine-containing alkyl group of $1 \sim 10$ carbons or a fluorine-containing alkyl group having ether bond; Z⁷ is an OH group or the group that changes to OH group by dissociating by the reaction with acid; Y¹, Y², Y³ are same or different and they are H, F, Cl, alkyl group of $1 \sim 10$ carbons, or a fluorine-containing alkyl group that may contain the ether bond of $1 \sim 10$ carbons; R's are same or different and they are H or alkyl group of $1 \sim 10$ carbons; n is an integer of $0 \sim 5$).

33. Chemically amplified photo resist composition described in Claim 32 where, in the structural unit M1a of the previously described fluorine-containing polymer (A), Y¹, Y² described in the previously described formula (16) are F and Y³ is F or CF₃.

34. Chemically amplified photo resist composition described in Claim 32 where, in the structural unit M1a of the previously described fluorine-containing polymer (A), Y¹, Y² described in the previously described formula (16) are F and Y³ is F or CF₃.

35. Chemically modified photo resist composition described in any one of Claims 32 ~ 34 where, in the structural unit M1a of the previously described fluorine-containing polymer (A), R⁶, R⁷ described in the previously described formula (16) are CF₃.

36. Chemically amplified photo resist composition described in any one of Claims 30 ~ 35 where, in the structural unit M1a of the previously described fluorine-containing polymer (A), the group Z⁷ that changes to OH by dissociating by reaction with acid is the group that is expressed by



(in the formulas, R¹, R², R³ and R⁴ are alkyl group of 1 ~ 5 carbons):

37. Chemically amplified photo resist composition described in any one of Claims 30 ~ 36 where the structural unit M2 of the previously described fluorine-containing polymer (A) is the structural unit that is obtained from at least one type of monomer selected from the group consisting of tetra fluoro ethylene and chloro trifluoro ethylene.

38. Chemically amplified photo resist composition described in Claim 29 that is a fluorine-containing polymer of number average molecular weight of 500 ~ 1000,000 having cyclic structure in the polymer main chain in which the previously described fluorine-containing polymer (A) is expressed by the formula (14)-2:



(in the formula, M1a-1 is the structural unit that originates from at least one selected from the norbornene derivative having the fluorine-containing alcohol structure described in any one of Claims 8 ~ 16; M1a-2 is the structural unit that originates from at least one selected from the norbornene derivative which has the protective acid reactive functional group described in Claim 17 or 18; M2 and N are same as formula (14)).

When (M1a-1) + (M1a-2) + M2 = 100 mol %, {(M1a-1) + (M1a-2)}/ M2 is in the mol % ratio of 30/70 ~ 70/30 and the structural unit M1a-a is contained by 1 ~ 98 mol %, structural unit M1a-2 by 1 ~ 98 mol %, structural unit M2 by 1 ~ 98 mol % and structural unit N by 0 ~ 97 mol %.

39. Chemically amplified photo resist composition described in Claim 38 in which, when (M1a-1) + (M1a-2) = 100 mol %, (M1a-1)/ (M1a-2) is in the mol % ratio of 90/10 ~ 50/50.

40. Chemically amplified photo resist composition described in Claim 29 which is characterized by that

the fluorine-containing polymer (A) is expressed by the formula (14)-3:

$$- (M1a-3) - (M2) - (N2) - (N) - \dots (14)-3$$

(in the formula,

structural unit M2 is same as formula (14);

structural unit M1a-3 is what originates from at least one selected from the norbornene derivative described in any one of Claims 8 ~ 18;

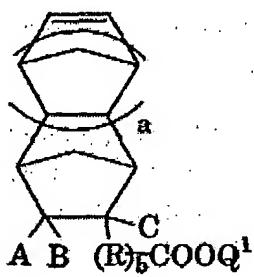
structural unit N2 consists of cyclic aliphatic unsaturated hydrocarbon that can copolymerize with the monomer that constitutes the structural unit M1a-3, M2 and N and, further, it originates from the cyclic aliphatic unsaturated hydrocarbon having COOH group or the acid-dissociating functional group that can be converted to carboxyl group by acid;

the structural unit N is what originates from the monomer that can copolymerize with the monomer that constitutes the structural unit M1a, M2 and N2);

and that, when $(M1a-3) + M2 + N2 = 100 \text{ mol \%}$, $\{(M1a-3) + N2\} / M2$ is in the mol % ratio of 70/30 ~ 30/70, structural unit M1a-3 is contained by 1 ~ 98 mol %, structural unit M2 by 1 ~ 98 mol %, structural unit N2 by 1 ~ 98 mol %, and structural unit N by 0 ~ 97 mol %.

41. Chemically amplified photo resist composition described in Claim 40 where, in the fluorine-containing polymer of formula (14)-3, the structural unit N2 is what originated from the norbornene derivative that has COOH group or the acid-dissociation functional group that can be converted to carboxyl group by acid.

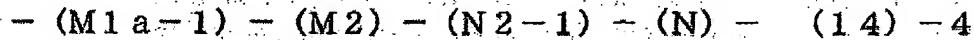
42. Chemically amplified photo resist composition described in Claim 41 in which the norbornene derivative that has COOH group or the acid-dissociation functional group which can be converted to carboxyl group by acid is expressed by the formula:



(in the formula, A, B and C are H, F, alkyl group of 1 ~ 10 carbons, or fluorine-containing alkyl group of 1 ~ 10 carbons; R is a divalent hydrocarbon group of 1 ~ 20 carbons, fluorine-containing alkylene group of 1 ~ 20 carbons or fluorine-containing alkylene group having ether bond of 2 ~ 100 ether bond; a is 0 or an integer of 1 ~ 3; b is 0 or 1;

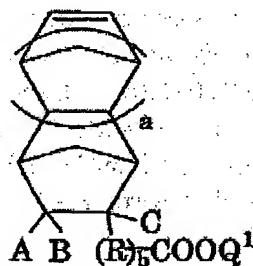
COOQ^1 is COOH group or the acid-dissociation functional group that can be converted to carboxyl group by acid. However, when b is 0 or R does not contain fluorine atom, any one of $A \sim C$ is fluorine atom or fluorine-containing alkyl group).

43. Chemically amplified photo resist composition described in Claim 29 in which the fluorine-containing polymer (A) is the fluorine-containing polymer that is expressed by the formula (14)-4:



(in the formula,

structural units M1a-1 and M2 are same as the formula (14)-2 described in Claim 38;
structural unit N2-1 is what originates from the norbornene derivative that is expressed by the formula:



(in the formula, COOQ^1 is the acid-dissociation functional group that can be converted to carboxyl group by acid);

structural unit N is that originates from the monomer that can copolymerized with the monomer which constitutes the structural units M1a-1 , M2 and N2-1 ;
and when $(\text{M1a-1}) + (\text{M2}) + (\text{N2-1}) = 100 \text{ mol \%}$, $(\text{M1a-1}) + (\text{N2-1}) / (\text{M2})$ is in the mol % ratio of $70/30 \sim 30/70$ and, also, when $(\text{M1a-1}) + (\text{N2-1}) = 100 \text{ mol \%}$, $(\text{M1a-1}) / (\text{N2-1})$ is in the mol % ratio of $95/5 \sim 50/50$; structural unit M1-1 is contained by $1 \sim 98 \text{ mol \%}$, structural unit M2 by $1 \sim 99 \text{ mol \%}$, structural unit N2-1 by $1 \sim 98 \text{ mol \%}$, structural unit N by $0 \sim 97 \text{ mol \%}$.

44. Chemically amplified photo resist described in any one of Claim 29 and Claims 38 ~ 43 in which the structural unit M2 is the structural unit that is obtained from at least one type of monomer selected from the group consisting of tetra fluoro ethylene, chloro trifluoro ethylene, vinylidene fluoride and vinyl fluoride.

45. Chemically amplified photo resist described in Claim 44 in which the structural unit M2 is the structural unit that is obtained from the tetra fluoro ethylene or chloro trifluoro ethylene.

Method of making fluorine-containing norbornene derivatives

Araki, T. et al of Daikin Kogyo K. K.

(Partial Translation of p. 124 ~ p. 188 of the original Japanese text)

The amount of this solvent (C) is selected by considering the type of solid component being dissolved, the substrate that is to be coated and the targeted film thickness. But, from the viewpoint of the ease of coating, it is preferred to use such an amount that the total solid content concentration of the resist composition is 0.5 ~ 70 wt %, preferably 1 ~ 50 wt %.

As for the method of using the chemically amplified resist composition of this invention, the method of forming the resist pattern by the existing photo resist technology is used. But, in order to conduct it properly, first the solution of the said resist composition is coated by using a spinner, etc. on the supporting body such as silicon wafer and this is dried to form the photo-sensitive layer and, to this, by using a reducing projection exposure apparatus, the UV ray, deep-UV, Excimer laser light, X ray is irradiated through the desired mask pattern or drawing is done by electron ray and heating is done. Next, this is given the development processing by using the alkaline aqueous solution such as 1 ~ 10 wt % tetra methyl ammonium hydroxide water solution. By this method of formation, one can obtain the picture image that is faithful to the mask pattern.

In particular, it was found out that, by using the chemically amplified resist composition of this invention, the resist coated film (photo-sensitive layer) having high degree of transparency can be formed even in the vacuum ultra violet zone. By this, it can be utilized preferably in the photolithography process that uses the F₂ laser (157 nm wavelength) which is being developed aiming particularly at the future 0.1 μm technology.

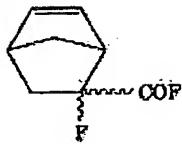
In the following, the invention is explained on the basis of the examples of synthesis and examples of application but this invention is not limited to these examples.

Synthesis Example 1

(Synthesis of norbornene that has the -COF group)

In a 500 ml glass flask having 4 openings and equipped with the reflux cooler, thermometer, stirrer and dropping funnel, 136 g of cyclo penta diene and 1.0 g of hydro quinone were charged and this was cooled to 0 ~ 5 deg C. Under the nitrogen gas stream, 233 g of α-fluoro acrylic acid fluoride (CH₂=CFCOF) was dropped taking 3 hours. After the dropping was finished, stirring was done for 3 hours at the room temperature.

From the reaction mixture, by vacuum distillation, 360 g (yield 90 %) of 5-norbornene-2-carboxylic acid fluoride which is a norbornene compound having the -COF group:



(melting point 73 ~ 75 deg C/ 45 mm Hg) was obtained.

For this compound, analyses were conducted by GC-Mass, ^{19}F -NMR and ^1H -NMR and the structure shown above was identified.

Example of Application 1

(Synthesis of ((5 – norbornene –2- yl) trifluoro methyl ketone)

In a 100 ml flask having 3 openings and equipped with a thermometer, cooling tube attached with a 3-way cock, and dropping funnel, 17 g (112 mmol) of 5 – norbornene –2- carboxylic acid methyl ester (mixture of endo and exo) and 0.45 g (3 mmol) of cesium fluoride were charged and this was cooled in an ice bath under nitrogen gas atmosphere. While keeping the temperature inside the flask at 3 ~ 10 deg C, under stirring, 22 g (156 mmol) of CF_3SiMe_3 was dropped taking 2 hours. Temperature was returned to the room temperature and stirring was done for 3 hours. Next, 2 g (8 mmol) of tetra butyl ammonium fluoride was added and stirring was done for 1 hour. The reaction solution was poured into ice water and extraction was conducted with diethyl ether. The organic phase was dried with calcium chloride and, after this, purification was done by vacuum distillation to obtain 12 g of (5 – norbornene –2- yl) trifluoro methyl ketone (yield 56 %, based on 5 – norbornene –2- carboxylic acid methyl ester).

This substance had the following physical properties.

^{19}F -NMR (solvent: CDCl_3): -78.0 (s, CF_3 , exo form), -78.3 (s, CF_3 , endo form)

MS: 190 (M^+), 121 ($\text{M}^+ - \text{CF}_3$), 66 (C_5H_6)

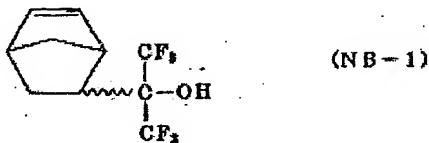
IR: 1753 cm^{-1} ($\text{C}=\text{O}$), 1574 cm^{-1} ($\text{C}=\text{C}$)

Example of Application 2

(Synthesis of ((5– norbornene –2- yl)- 1, 1, 1, 3, 3, 3 –hexa fluoro–2- propanol (NB-1))

In a 100 ml flask having 3 openings and equipped with a thermometer, the cooling tube attached with a 3-way cock, and dropping funnel, 12 g (64 mmol) of (5-norbornene-2-yl) trifluoro methyl ketone (mixture of endo and exo), 11 g of CF_3SiMe_3 (79 mmol) and 20 ml of THF were charged and this was cooled in a dry ice acetone bath under the nitrogen gas atmosphere. While keeping the temperature inside the flask below -70 deg C, under stirring, 3 ml of 1 M THF solution of tetra butyl ammonium fluoride was dropped slowly. The flask was returned to the room temperature and, after this, 20 ml of 5 % hydrochloric acid was added and further stirring was done for 3 hours. Extraction was done with diethyl ether and washing was done with saturated sodium bicarbonate

water solution. After this, the organic phase was dried with calcium chloride. After distilling out the solvent, purification was conducted by vacuum distillation to obtain 11g (yield 65 %, based on (5-norbor-nene -2- yl) trifluoro methyl ketone) of (5- norbornene -2- yl) - 1, 1, 1, 3, 3, 3 – hexa fluoro -2- propanol (NB-1).



NB-1 had the following physical properties.

$^{19}\text{F-NMR}$ (solvent: CDCl_3): -74.0 (q, CF_3 , endo form), -74.9 (q, CF_3 , exo form), -75.3 (q, CF_3 , endo form), -76.8 (q, CF_3 , exo form)

MS: 260 (M^+), 1991 ($\text{M}^+ - \text{CF}_3$), 125, 97, 66 (C_5H_6)

IR: 3510 cm^{-1} (O-H), 1579 cm^{-1} (C=C)

Example of Application 3

(One pot synthesis of (5 – norbornene -2- yl) – 1, 1, 1, 3, 3, 3 – hexa fluoro -2- propanol (NB-1))

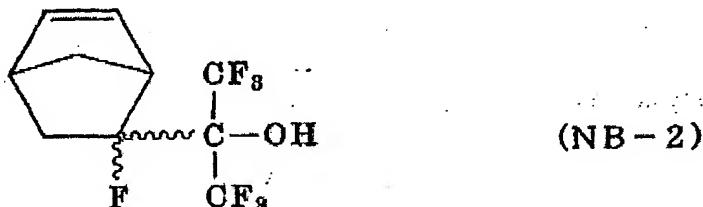
In a 100 ml flask having 3 openings and equipped with the cooling tube attached with a thermometer, 3-way cock, and dropping funnel, 1.3 g (8.5 mmol) of 5 – norbornene -2- carboxylic acid methyl ester (mixture of endo and exo), 6.1 g (43 mmol) of CF_3SiMe_3 and 15 ml of hexane were charged and this was cooled in an ice bath under the nitrogen gas atmosphere. While keeping the flask temperature at 3 ~ 10 deg C, under stirring, 2 ml (2 mmol) of 1M THF solution of tetra butyl ammonium fluoride was added slowly taking more than 4 hrs. Flask was returned to the room temperature and stirring was done for 24 hours. After this, the reaction solution was analyzed: 5 – norbornene -2- carboxylic acid methyl ester was 28 %, (5 – norbornene -2- yl) – 1, 1, 1, 3, 3, 3 – hexa fluoro -2- propanol (NB-1) was 20 %.

Example of Application 4

(One pot synthesis of (2 – fluoro -5- norbornene -2- yl) – 1, 1, 1, 3, 3, 3 – hexa fluoro -2- propanol (NB – 2))

In a 100 ml flask having 3 openings and equipped with a thermometer, a cooling tube attached with a 3-way cock, and a dropping funnel, 27.7 g (168 mmol) of the 5 – norbornene -2- carboxylic acid fluoride (mixture of endo and exo) that was synthesized in the Synthesis Example 1 and 28 g (482 mmol) of potassium fluoride were charged and this was cooled in an ice bath under the nitrogen gas atmosphere. While keeping the temperature inside the flask at 3 ~ 10 deg C, under stirring, 62 g (436 mmol) of CF_3SiMe_3 was dropped taking 2 hours. Temperature was returned to the room temperature and stirring was done for one night. The reaction solution was poured into the ice water and extraction was conducted with diethyl ether. The organic phase was washed with water, with

dilute hydrochloric acid and, in continuation, with saturated sodium bicarbonate water. After this, the organic phase was dried with calcium chloride. Purification was conducted by vacuum distillation to obtain 50 g (yield 80 %) of (2 - fluoro -5- norbornene -2- yl) - 1, 1, 1, 3, 3, 3 - hexa fluoro -2- propanol (NB - 2).



NB-2 had the following physical properties.

¹⁹F-NMR (solvent: CDCl₃):

endo form: -156.7 (m, F), -72.3 (m, CF₃), -72.0 (m, CF₃)

exo form: -152.2 (m, F), -73.8 (m, CF₃), -72.5 (m, CF₃)

¹H-NMR (solvent: CDCl₃): 6.60 – 6.23 (1H, m, sp²CH), 6.10 – 5.86 (1H, m, sp²CH), 4.34 – 3.80 (1H, s broad, OH), 3.80 – 3.47 (m, 1H), 3.37 – 2.98 (1H, s), 2.5 – 2.15 (1H, t), 2.10 – 1.61 (2H, m)

MS: 241 (M⁺ - FH₂O), 22.1 201, 66 (C₅H₆)

IR: 3500 cm⁻¹ (O-H, 1590 cm⁻¹ (C = C)

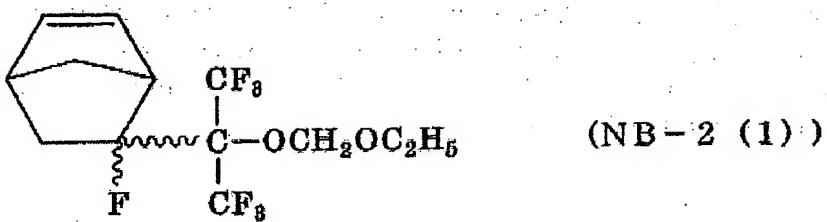
Example of Application 5

(Introduction of the protective group)

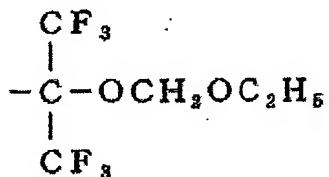
In a 100 ml flask with 4 openings and equipped with the reflux cooler, thermometer, stirrer, and dropping funnel, 3.5 g of sodium hydride (purity 60 %) and 10 ml of tetra hydro furan were charged and, while keeping the inside temperature at 5 ~ 10 deg C, 2.1 g of the norbornene having the -C(CF₃)₂OH group (NB-2) that was prepared in Example of Application 4 was dropped taking 1 hour. After the dropping was finished, at the room temperature, stirring was done for 1.5 hours. Next, 9.6 g of chloro methyl ethyl ether (ClCH₂OC₂H₅) was dropped taking 1 hour. After the dropping was finished, stirring was done for 5 hours at the room temperature.

After the reaction was finished, water was added and the organic substance was extracted by ether and the ether layer was washed with saturated NaHCO₃ water and drying was done with anhydrous magnesium sulfate.

After the drying, ether was distilled out and, by vacuum distillation, 20.5 g (yield 77 %) of the norbornene compound (NB-2 (1)):



(melting point 58 ~ 61 deg C/ 1.5 mmHg) which has the group



was obtained.

For this compound, analyses were conducted by GC - Mass, ^{19}F -NMR and ^1H - NMR and the structure shown above was identified.

Synthesis Example 2

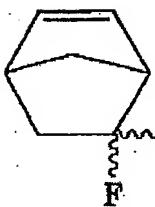
(Synthesis of the norbornene (NBC -1) that has the $-\text{COOC}(\text{CH}_3)_3$ group)

In a 300 ml flask having 4 openings and equipped with a reflux cooler, thermometer, stirrer, and dropping funnel, 61 g of cyclo penta diene, 26 g of t- butyl - α - fluoro acrylate, 50 ml of tetra hydro furan and 0.1 g of hydro quinone were charged and the inside temperature was kept at 25 deg C.

Under the nitrogen gas stream, while stirring, 4.0 g of boron trifluoride – diethyl ether complex was dropped and, after the dropping was finished, stirring was done for 48 hours at the room temperature for the reaction.

After the reaction was finished, tetra hydro furan was distilled out by distillation and the residue was taken out and water was added and the organic substance was extracted by methylene chloride. The methylene chloride layer was washed with 5 % NaHCO_3 water and drying was done by anhydrous magnesium sulfate.

After the drying, the organic layer was separated and methylene chloride was distilled out and, after this, by vacuum distillation, 14 g of norbornene (NBC-1) having the $-\text{COOC}(\text{CH}_3)_3$ group which is an acid reactive group



(N B C - 1)

(melting point 70 ~ 72 deg C / 2 mm Hg) was obtained.

For this compound, analyses were conducted by GC - Mass, ^{19}F -NMR and ^1H -NMR and the structure shown above was identified.

Example of Application 6

(Synthesis of the copolymer of TFE and the fluorine- containing norbornene containing OH group (NB-2))

In a 300 ml autoclave equipped with a valve, pressure gauge and thermometer, 20.7 g of the fluorine- containing norbornene that contains OH group (NB-2) which was prepared in Example of Application 4, 140 ml of HCFC - 141b, and 1.5 g of bis (4 - t - butyl cyclo hexyl) peroxy dicarbonate (TCP) were charged and, while cooling with dry ice/ methanol solution, inside of the system was thoroughly purged with nitrogen gas. Next, through the valve, 30.0 g of TFE was charged and, at 40 deg C for 12 hours, reaction was let to occur by penetration. With the progress of reaction, the gauge pressure dropped from 0.96 MPa G (9.7 kgf/ cm² G) before the reaction to 0.91 MPa G (9.2 kgf/ cm² G).

After discharging the unreacted monomer, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted until the weight reached a constant value to obtain 4.1 g of the copolymer.

According to the results of analyses by ^1H -NMR and ^{19}F -NMR, the composition ratio of this copolymer was TFE/ the said fluorine- containing norbornene derivative containing OH group (NB-2) = 50/ 50 mol %.

By the GPC analysis, the number average molecular weight was 3500.

Example of Application 7

(Synthesis of the copolymer of TFE and the fluorine- containing norbornene that contains OH group (NB-1))

In Example of Application of 6, in place of the fluorine- containing norbornene derivative that contains OH group which was prepared in Example of Application 4; 19.3 g of the fluorine- containing norbornene that contains OH group (NB-1) which was prepared in Example of Application 2 was used. Other than this, the reaction was conducted in the

same manner as in Example of Application 6. With the progress of reaction, the gauge pressure dropped from 0.95 MPa G before the reaction to 0.92 MPa G.

After the unreacted monomer was discharged, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted and the weight reached a constant value to obtain 3.7 g of the copolymer.

According to the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, the composition ratio of this copolymer was TFE/ the said fluorine- containing norbornene derivative containing OH group (NB-1) = 50/ 50 mol %.

By the GPC analysis, the number average molecular weight was 3400.

Example of Application 8

(Synthesis of the copolymer of TFE and the fluorine- containing norbornene that contains $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB-2 (1)))

In Example of Application of 6, in place of the fluorine- containing norbornene derivative that contains OH group which was prepared in Example of Application 4, 26.2 g of the fluorine- containing norbornene that contains $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB-2(1)) which was synthesized in Example of Application 5 was used. Other than this, the reaction was conducted in the same manner as in Example of Application 6. With the progress of reaction, the gauge pressure dropped from 0.94 MPa G (9.5 kgf/ cm² G) before the reaction to 0.91 MPa G (9.2 kgf/ cm² G). Then, the separation and purification were conducted in the same manner as in Example of Application 6 to obtain 3.9 g of the copolymer.

According to the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, the composition ratio of this copolymer was TFE/ the said fluorine- containing norbornene derivative containing $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB-2 (1)) = 50/ 50 mol %.

By the GPC analysis, the number average molecular weight was 2600.

Example of Application 9

(Synthesis of the copolymer of TFE and the fluorine- containing norbornene that contains $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB-2 (1)) and 2- norbornene)

In Example of Application of 6, in place of the fluorine- containing norbornene derivative that contains OH group which was prepared in Example of Application 4, 18.5 g of the fluorine- containing norbornene that contains $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB- 2(1)) which was synthesized in Example of Application 5 and 2.1 g of 2- norbornene were used. Other than this, the reaction was conducted in the same manner as in Example of Application 6. Then, the separation and purification were conducted in the same manner as in Example of Application 6 to obtain 4.3 g of the copolymer.

According to the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, the composition ratio of this copolymer was TFE/ the said fluorine- containing norbornene derivative containing $-\text{OCH}_2\text{OC}_2\text{H}_5$ group (NB-2 (1))/ 2- norbornene = 56/ 31/ 13 mol %.

By the GPC analysis, the number average molecular weight was 3200.

Example of Application 10

(Synthesis of the copolymer of TFE and the fluorine- containing norbornene that contains $-\text{OH}$ group (NB-2) and the fluorine- containing norbornene derivative that contains $-\text{COOC}(\text{CH}_3)_3$ group (NBC-1))

In a 500 ml autoclave equipped with a valve, pressure gauge, stirrer and thermometer, 3.1 g of the fluorine- containing norbornene derivative that contains $-\text{OH}$ group and was prepared in Example of Application 4, 21.0 g of the fluorine- containing norbornene derivative containing $-\text{COOC}(\text{CH}_3)_3$ group and was synthesized in Synthesis Example 2 (NBC-1), 250 ml of HCFC - 141b and 6.6 g of bis (4 - t - butyl cyclo hexyl) peroxy dicarbonate (TCP) were charged and the inside of system was thoroughly purged with nitrogen gas. Then, 44g of TFE was charged from the valve and, at 40 deg C, reaction was conducted by penetration for 12 hours.

After the unreacted monomer was discharged, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted and the weight reached a constant value to obtain 6.9 g of the copolymer.

According to the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, the composition ratio of this copolymer was TFE/ the said fluorine- containing norbornene derivative containing OH group (NB-2)/ fluorine-containing norbornene derivative containing $-\text{COOC}(\text{CH}_3)_3$ group (NBC-1) = 54/ 9.2/ 36.8 mol %.

By GPC analysis, the number average molecular weight was 2800.

(At this point, the translator was instructed to go to the claims for translation, omitting the remaining part of the text from the translation).

CK for Rose Ann

Examples

WO 03 / 006413

(Partial Translation, into Japanese, from p. 133; Example of Application 11 to p. 167)

Example of Application 11

(Synthesis of the copolymer of TFE and the fluorine-containing norbornene derivative containing -OH group (NB-2) and the fluorine-containing norbornene derivative containing -COOC(CH₃)₃ group (NBC-1))

In Example of Application 10, 9.2 g of the fluorine-containing norbornene derivative containing OH group (NB-2) that was made in Example of Application 4 and 16.3 g of the fluorine-containing norbornene derivative containing -COOC(CH₃)₃ group (NBC-1) that was synthesized in the Synthesis Example 2 were used. Other than these, the same procedure as in Example of Application 10 was followed to conduct the reaction. Next, the purification by separation was conducted in the same way as in Example of Application 10 to obtain 7.2 g of the copolymer.

As to the composition ratio of this copolymer, by the results of analyses by ¹H-NMR and ¹⁹F-NMR, the copolymer had the TFE / the fluorine-containing norbornene derivative containing -OH group (NB-2) / the fluorine-containing norbornene derivative containing -COOC(CH₃)₃ group (NBC-1) ratio of 52/ 29/ 19 mol %.

By the GPC analysis, the number average molecular weight was 3300.

Example of Application 12

(Measurement of the transparency at the wavelength of 157 nm)

(1) Preparation of the coating composition

The fluorine-containing polymers of various types that were made in Examples of Application 6 ~ 11 were dissolved in butyl acetate to the concentration of 3 % to prepare the coating composition.

(2) Coating

[1] Coating on the substrate (MgF₂) for use in the measurement of transparency

On the substrate of MgF₂, each of the coating compositions was coated by using the spin coater at room temperature under the condition of 1000 rotations. After the coating, baking was done for 15 minutes at 100 deg C to prepare the transparent coated film.

[2] Measurement of film thickness

Silicone wafer was used in place of the MgF₂ substrate. Other than this, under the same conditions described above, each of the coating compositions was used to form coated film on the silicone wafer.

By using the AF apparatus (Seiko Denshi (K. K.) SPI 3800), thickness of the coated film was measured. Results are shown in Table 1.

(3) Measurement of transparency of the ultraviolet region in vacuum

[1] Apparatus of Measurement

- o Spectroscopic apparatus of Setani – Namioka (High Energy Research Mechanism: BL-7B)
- o Slit 7/8 – 7/8
- o Detector: PMT
- o Grating (GII: blazed wavelength 160 nm; 1200 ea./ mm)

As for the optical system, see H. Namba, et al. Rev. Sci. Instrum., 60 (7), 1917 (1989).

[2] Measurement of transmission spectrum

For the coated film formed on the MgF₂ substrate that was obtained by the method of (2) – [1], the transmission spectrum of 200 ~ 100 nm was measured by using the apparatus described above.

From the transmittance at 157 nm and the film thickness of the coated film, the molecular extinction coefficient was calculated. This is shown in Table 1.

Example of Application 13

(Evaluation of the etching resistance)

10 % butyl acetate solution of the fluorine-containing polymers that were prepared in Examples of Application 6 ~ 11 were prepared and this was coated on the Si substrate by using a spin coater to a film thickness of 200 nm. This was pre-baked at 120 deg C for 2 minutes and, after this, by using an interference film thickness meter, the film thickness was measured. After this, it was placed in a chamber of the ICP (induction-coupled plasma) etching apparatus and etching was conducted. Pressure of the etching gas (Ar/N₂/C₄F₈ mixed gas) was 10 mTorr, and the plasma condition was: upper electrode 13.56 MHz, 900 W, lower electrode 400 kHz, 100W. Etching time was 60 seconds.

The film thickness after the etching was measured by an interference film thickness meter and the etching rate was calculated. As the reference, the etching rate was determined similarly by using the resist (Tarf-6a – 63) made by Tokyo Ohka (K. K) which is used in the lithography for ArFlaser, and the etching rate is given by the comparison with

it. Thus, each numerical value is given by the ratio, taking the etching rate of the reference polymer (ArF laser resist mentioned above) as 1.

Example of Application 14

(Evaluation of the solubility to the development solution)

(1) Separation reaction of the protective group

By using the fluorine-containing polymer of Examples of Application 6 ~ 11, reaction with the trifluoro acetic acid was conducted using dichloro methane solvent and, by this, the various types of protective group contained in the fluorine-containing polymer was separated.

¹H-NMR and IR analysis were conducted to confirm that more than 85 % of protective group was separated and converted to OH group or COOH group.

(2) Coating

10 % butyl acetate solutions of the fluorine-containing polymer obtained in Examples of Application 6 ~ 11 and the fluorine-containing polymer after the separation of protective group obtained above were prepared and this was coated by spin coater on the Si substrate to a film thickness of 200 nm and this was dried.

(3) Checking of the solubility

The Si substrate after drying was dipped for 60 seconds in the 2.38 % tetra methyl ammonium hydroxide water solution. After this, the whole substrate was taken out and this was dried at the room temperature and the presence or absence of the remaining film was checked visually.

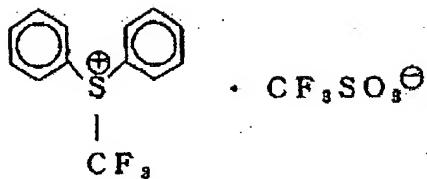
For the case where the film did not remain, the solubility was rated as O. Results are shown in Table 1.

Example of Application 15

(1) Preparation of the coating compositions

The fluorine-containing polymer (A) that was made in Examples of Application 8 ~ 11 and the Kosan (photo oxide acid?) generating agent (B) by an amount that is 5 wt % with respect to the polymer (A) were dissolved in butyl acetate as the solvent (C) for diluting the polymer concentration to 5 wt %.

As for the Kosan generating agent, S- (trifluoro methyl) - dibenzo thiophenium trifluoro methane sulfonate



was used.

(2) Coating

Coating was done with a spin coater on the Si substrate to a film thickness of 200 nm.

(3) Measurement of the transparency of the ultraviolet region in vacuum

The same procedure as in Example of Application 12 was followed. The molecular extinction coefficient at 157 nm is shown in Table 1.

Table 1.

Fluorine-containing polymer	Example of Application 12 Extinction coefficient at 157 nm (μm^{-1})	Example of Application 13 Etching grade (to ArF resist)	Example of Application 14 Solubility to the development solution Before separating protective group	Example of Application 14 After separating protective group	Example of Application 15 Extinction coefficient at 157 nm (μm^{-1})
EA* 6	1.4	0.92	O	-	1.6
EA 7	1.8	0.96	O	-	2.0
EA 8	1.9	0.82	X	O	2.2
EA 9	2.0	0.86	X	O	2.3
EA 10	2.8	0.93	X	O	3.0
EA 11	2.3	0.90	O	O	2.5

*EA: Example of Application

Example of Application 16 (Synthesis of the copolymer of TFE and the fluorine-containing norbornene that contains OH group (NB-2))

In a 500 ml autoclave equipped with a valve, pressure gauge, stirrer and thermometer, 35.0 g of the fluorine-containing norbornene that contains OH group (NB-2) which was obtained in Example of Application 4, 250 ml of HCFC- 141b, and 6.5 g of bis (t-4-butyl cyclo hexyl) peroxy dicarbonate (TCP) were placed and, while cooling with the dry ice / methanol solution, inside of the system was purged thoroughly with nitrogen gas. Next, from the valve, 52.0 g of TFE was charged and, at 40 deg C, for 12 hours, reaction was let to occur by stirring. With the progress of the reaction, the gauge pressure dropped from 0.96 MPa G (9.7 kgf/cm² G) before the reaction to 0.91 MPa G (9.2 kgf/cm² G).

After the unreacted monomer was discharged, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted until a constant weight was reached and 6.0 g of copolymer was obtained. In the result of analyses by ¹H-NMR and ¹⁹F-NMR,

composition ratio of this copolymer was TFE / the said fluorine- containing norbornene derivative that contains OH group (NB-2) was 50/ 50 mol %.

By the GPC analysis, the number average molecular weight was 5500.

Example of Application 17 (Synthesis of the copolymer of TFE and the fluorine- containing norbornene derivative that contains $-OCH_2OC_2H_5$ group (NB-2(1))

In Example of Application 16, in place of the fluorine- containing norbornene derivative that contains OH group (NB-2) which was obtained in Example of Application 4, 40.0 g of the fluorine- containing norbornene derivative that contains $-OCH_2OC_2H_5$ group (NB-2(1)) which was obtained in Example of Application 5 was used. Other than this, the same procedure as in Example of Application 16 was followed to conduct the reaction. With the progress of reaction, the gauge pressure dropped from 0.94 MPa G (9.5 kgf/ cm² G) to 0.91 MPa G (9.2 kgf/ cm² G). Next, purification was done by separation in the same way as in Synthesis Example 1 and 7.5 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE / the said fluorine- containing norbornene derivative that contains the $-OCH_2OC_2H_5$ group (NB-2(1)) was 50/ 50 mol %.

By the GPC analysis, the number average molecular weight was 4600.

Example of Application 18 (Synthesis of the copolymer of TFE, the fluorine- containing norbornene derivative that contains OH group (NB-2) and the fluorine- containing norbornene derivative that contains $-OCH_2OC_2H_5$ group (NB-2(1))

In a 500 ml autoclave equipped with a valve, pressure gauge, stirrer and thermometer, 18.3 g of the fluorine- containing norbornene derivative that contains $-OH$ group which was obtained in Example of Application 4 (NB-2), 14.8 g of the fluorine- containing norbornene derivative that contains $-OCH_2OC_2H_5$ group (NB-2(1)) which was obtained in Example of Application 5, 250 ml of HCFC-141b and 6.6 g of bis (4 -t- butyl cyclo hexyl peroxy dicarbonate (TCP) were charged and inside of the system was purged thoroughly with nitrogen gas. Next, from the valve, 52.0 g of TFE was charged and, at 40 deg C, for 12 hours, the reaction was let to go by stirring.

After the unreacted monomer was discharged, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 6.9 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE / fluorine- containing norbornene derivative that contains $-OH$ group (NB-2)/ fluorine- containing norbornene derivative that contains the $-OCH_2OC_2H_5$ group (NB-2(1)) was 50/ 19/ 31 mol %.

By the GPC analysis, the number average molecular weight was 3000.

Example of Application 19 (Synthesis of the copolymer of TFE, the fluorine-containing norbornene derivative that contains OH group (NB-2) and the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1))

In Example of Application 18, 24.5 g of the fluorine-containing norbornene derivative that contains -OH group (NB-2), 7.4 g of the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)), 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 18 was followed to conduct the polymerization reaction, separation and purification of the polymer and 7.2 g of the polymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE / fluorine-containing norbornene derivative that contains -OH group (NB-2)/ fluorine-containing norbornene derivative that contains the -OCH₂OC₂H₅ group (NB-2(1)) was 50/ 40/ 10 mol %.

By the GPC analysis, the number average molecular weight was 3200.

Example of Application 20 (Synthesis of the copolymer of TFE, the fluorine-containing norbornene derivative that contains OH group (NB-2) and the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1))

In Example of Application 18, 27.5 g of the fluorine-containing norbornene derivative that contains -OH group (NB-2), 3.7 g of the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)), 52.0 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 18 was followed to conduct the polymerization reaction, separation and purification of the polymer and 7.6 g of the polymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE / fluorine-containing norbornene derivative that contains -OH group (NB-2)/ fluorine-containing norbornene derivative that contains the -OCH₂OC₂H₅ group (NB-2(1)) was 50/ 46/ 4 mol %.

By the GPC analysis, the number average molecular weight was 3500.

Example of Application 21 ((Synthesis of the copolymer of TFE, the fluorine-containing norbornene derivative that contains OH group (NB-2) and the fluorine-containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-1)

In a 500 ml autoclave equipped with a valve, pressure gauge, stirrer and thermometer, 24.5 g of the fluorine-containing norbornene derivative that contains -OH group which was obtained in Example of Application 4 (NB-2), 4.7 g of the fluorine-containing nor-

bornene derivative that contains $-COOC(CH_3)_3$ group (NBC-1) which was obtained in Synthesis Example 2, 250 ml of HCFC-141b and 6.5 g of bis (4 -t- butyl cyclo hexyl peroxy dicarbonate (TCP) were charged and inside of the system was purged thoroughly with nitrogen gas. Next, from the valve, 52.0 g of TFE was charged and, at 40 deg C, for 12 hours, the reaction was let to go by stirring.

After the unreacted monomer was discharged, the polymerization solution was taken out and, after concentrating, re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 6.9 g of the copolymer was obtained.

In the results of analyses by 1H -NMR and ^{19}F -NMR, composition ratio of this copolymer was TFE / fluorine- containing norbornene derivative that contains $-OH$ group (NB-2)/ fluorine- containing norbornene derivative that contains the $-COOC(CH_3)_3$ group (NBC-1) was 50/ 40/ 10 mol %.

By the GPC analysis, the number average molecular weight was 3800.

Example of Application 22 ((Synthesis of the copolymer of TFE, the fluorine- containing norbornene derivative that contains OH group (NB-2) and the fluorine- containing norbornene derivative that contains $-COOC(CH_3)_3$ group (NBC-1))

In Example of Application 21, 27.5 g of the fluorine- containing norbornene derivative that contains OH group (NB-2), 2.3 g of the fluorine- containing norbornene derivative that contains $-COOC(CH_3)_3$ group (NBC-1), 52.0 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 21 was followed to conduct the polymerization reaction, separation and purification of the polymer and 7.3 g of the polymer was obtained.

In the results of analyses by 1H -NMR and ^{19}F -NMR, composition ratio of this copolymer was TFE / fluorine- containing norbornene derivative that contains $-OH$ group (NB-2)/ fluorine- containing norbornene derivative that contains the $-COOC(CH_3)_3$ group (NBC-1) was 50/ 47/ 3 mol %.

By the GPC analysis, the number average molecular weight was 4000.

Example of Application 23 (Synthesis of the copolymer of TFE and the fluorine- containing norbornene that contains OH group (NB-1))

In Example of Application 16, in place of the fluorine- containing norbornene that contains OH group (NB-2), 32.5 g of the norbornene containing OH group (NB-1) that was obtained in Example of Application 2 was used. Other than this, the same procedure as in Example of Application 16 was followed to conduct the polymerization reaction, separation and purification of the polymer and 4.5 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was TFE / fluorine- containing norbornene that contains -OH group (NB-1) was 50/50 mol %.

By the GPC analysis, the number average molecular weight was 3800.

Example of Application 24 (Measurement of transparency at the wavelength of 157 nm)

Using the fluorine- containing polymers which were obtained in Examples of Application 16 ~ 23, respectively, (1) Preparation of the coating composition, (2) Coating, (3) Measurement of the transparency of the ultraviolet region in vacuum, were conducted. Molecular extinction coefficient at 157 nm is shown in Table 2.

Example of Application 25 (Evaluation of etching resistance)

Using the fluorine- containing polymers which were obtained in Examples of Application 16 ~ 23, respectively, evaluation of etching resistance was conducted in the same way as in Example of Application 13. Results are shown in Table 2.

Example of Application 26 (Evaluation of the solubility to the development solution)

Using the fluorine- containing polymers which were obtained in Examples of Application 16 ~ 23, (1) Reaction of separation of the protective group, (2) Coating, and (3) Checking of the solubility, were conducted. Results are shown in Table 2.

Example of Application 27

Using the fluorine- containing polymer (A) of Examples of Application 16 ~ 23, (1) Preparation of the resist composition, (2) Coating, and (3) Measurement of the transparency in the ultraviolet region in vacuum, were conducted in the same way as in Example of Application 14. Results are shown in Table 2.

Table 2.

Fluorine-containing polymer	Example of Application 24 Extinction coefficient at 157 nm (μm^{-1})	Example of Application 25 Etching grade (to ArF resist)	Example of Application 26 Solubility to the development solution Before separating protective group After separating protective group	Example of Application 27 Extinction coefficient at 157 nm (μm^{-1})
EA**1 6	1.1	1.19	O	1.3
EA 17	1.2	1.15	X	1.4
EA 18	1.1	1.15	X	1.4
EA 19	0.8	1.18	X	1.1
EA 20	1.0	1.13	A*	1.3
EA 21	1.9	1.07	X	2.2
EA 22	1.6	1.02	A*	1.8
EA 23	1.6	1.00	O	1.8

Table 2, continued

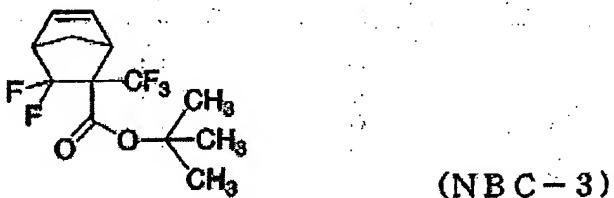
* A: Partially dissolving

**EA: Example of Application

Synthesis Example 3 (Synthesis of the fluorine-containing norbornene derivative that contains $-COOC(CH_3)_3$ group (NBC-3))

A 2 liter flask having 4 openings and equipped with a magnetic stirring element, dropping funnel, 3-way cock and thermometer was purged with nitrogen and 117 ml of $HN(Si(CH_3)_3)_2$ (0.55 mol) and 200 ml of TFE were added. This was cooled with dry ice – acetone bath and 328 ml (0.525 mol) of 1.6 N n-BuLi hexane solution was dropped taking 45 minutes such that the solution temperature would not exceed -50 deg C. Further stirring was done for 30 minutes and, after this, the solution obtained by dissolving 136 g (0.5 mol) of the benzoic acid (1, 1, 1; 3, 3, 3 – hexa fluoro -2- propyl) that was synthesized by the normal method in 200 ml of THF was dropped taking 45 minutes such that the solution temperature would not exceed 50 deg C. Then, further stirring was done for 30 minutes. Into the slurry prepared by adding 300 g of ice and 150 ml of concentrated hydrochloric acid in a 3 liter beaker and stirring, the reaction solution was slowly poured. Using a separating funnel, the organic layer was separated and the water layer was extracted 2 times with 300 ml of n-hexane. The 2 times extracted component was put together with the organic layer and this was washed with saturated table salt water. After drying with $MgSO_4$, concentrating was done by using an evaporator and purification was done by vacuum distillation. By this, 107.3 g of benzoic acid (1, 1, 1, 3, 3 – penta fluoro -2- propenyl) was synthesized. (Boiling point 71 ~ 73 deg C/ 24 mmHg).

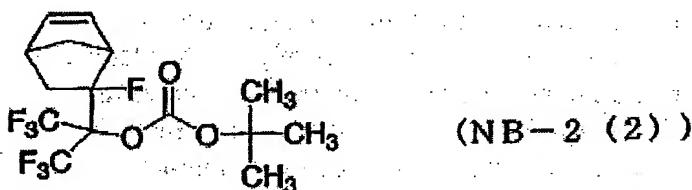
In a 500 ml autoclave made of SUS, 65 g (0.257 mol) of benzoic acid (1, 1, 1, 3, 3 – penta fluoro -2- propenyl), 22 g (0.167 mol) of di cyclo penta diene, and 0.73 g (6.6 mmol) of p- hydroxy quinone were charged and the autoclave was cooled with the dry ice – acetone bath and then it was purged with nitrogen. By using a heater, heating was done to raise the solution temperature to 170 deg C. After heating and stirring for 5 hours, the temperature was returned to the room temperature. Then the crude product was transferred to a 3 liter beaker and dissolved in 0.6 ml of methanol. While cooling with an ice bath, stirring was done by a magnetic stirring element and 0.2 liters of 4N-NaOH was added slowly. After stirring for 30 minutes at the room temperature, 0.6 liters of water was added to this and the alkaline water layer was washed with 300 ml of n-hexane. To the alkaline water layer, concentrated hydrochloric acid was added until the pH became 1 and the separated organic layer was taken out and this was dried with $MgSO_4$. The organic layer obtained was refined by vacuum distillation to obtain 48.4 g of the desired norbornene derivative (NBC-3) (Melting point 55 ~ 59 deg C/ 3 mm Hg).



By the ^{19}F -NMR, 1H -NMR, ^{13}C -NMR, and IR analysis, the monomer shown above was identified and confirmed.

Example of Application 28 (Synthesis of norbornene derivative (NB-2(2)))

In a 500 ml beaker, 180 ml of methylene chloride, 50 g (0.18 mol) of norbornene derivative containing OH group (NB-2), 51.1 g (0.23 mol) of $((\text{CH}_3)_3\text{OCOO})_2$ were charged and this was stirred at the room temperature. To this, 1.1 g (5 mol) of dimethyl amino pyridine was added. When the addition was started, gas started to be generated slowly. For about 1 hour thereafter, stirring was done until the generation of the gas stopped. After the reaction was finished, the organic layer was washed once with each of the pure water and saturated table salt water, in sequence. The organic layer obtained was dried overnight with Na_2SO_4 and then it was concentrated. By distilling this, the norbornene derivative (NB-2(2)) was obtained (Amount recovered 55 g, boiling point 76 deg C /0.05 mmHg).



By the ¹⁹F-NMR, ¹H-NMR, ¹³C-NMR, and IR analysis, the monomer shown above was identified and confirmed.

Example of Application 29 (Synthesis of norbornene derivative (NB-3))

A 1 liter flask was made vacuous and was purged with nitrogen and, next, into the still, 115 g (1.76 mol) of zinc powder and 400 ml of dehydrated DMF were charged. In a dropping funnel, 208 g (0.8 mol) of CF_3CFBr_2 , 100 ml of dehydrated DMF were charged and, under the nitrogen atmosphere, heating and stirring were conducted. After this, while maintaining 80 ~ 90 deg C, dropping was done by taking 2 hours and, next, at 90 ~ 95 deg C, for 4.5 hours, heating and stirring were done.

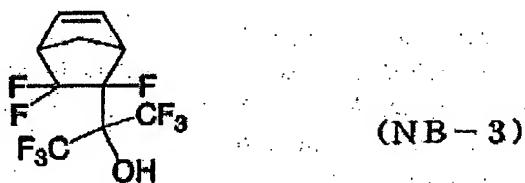
Dimroth was changed to dry ice acetone condenser and, while cooling the still, at the room temperature, CF_3COCF_3 was let in as gas. The feeding of CF_3COCF_3 was finished at the time point when the reflux has not stopped and the reaction was believed not to occur any more. The amount of feed was 92 g (0.55 mol). After this, by heating and pulling vacuum, the unreacted CF_3COCF_3 was removed and then diethyl ether was added and the organic layer was washed with 1N- hydrochloric acid and drying with CaCl_2 was conducted.

Purification by rectification by using the rectifying tower filled with packing material was conducted and, as the result, 56.6 g of the mixed solution consisting of 48.6 % of 1,1 - bis trifluoro methyl - 2, 3, 3 -trifluoro - 2- propene - 1- ol [$\text{CF}_2 = \text{CFC}(\text{CF}_3)_2\text{OH}$] and 47.0 % of diethyl ether, in terms of the GC area ratio, was obtained.

Solvent
¹⁹F-NMR (溶媒: CDCl₃): -77.0 (6F, q), -91.6 (1F, dd), -106.8 (1F, m), -184.1 (1F, m)
MS : 248(M⁺), 209, 181, 179, 159, 109, 69(CF₃), 31(CF)

In a 100 ml autoclave equipped with a pressure gauge, safety valve and stirrer, 45 g (150 mmol) of the diethyl ether solution of the 1, 1 - bis trifluoro methyl - 2, 3, 3 - trifluoro - 2- propene - 1- ol of the above said composition and 9.9 g (75 mmol) of cyclo penta diene dimer, 0.5 g of hydroquinone were charged and, at 170 deg C, for 24 hours, heating and stirring were done.

The crude product was transferred to a 1 liter beaker and, while cooling with an ice bath, stirring was done with a magnetic stirring element and 0.1 liter of 2N - NaOH water solution was added slowly. At room temperature, stirring was done for 30 minutes and, after this, 0.6 liter of water was added to it and the alkaline water layer was washed for several times with 100 ml of n-hexane. Further, this water layer was treated under a reduced pressure and, by this, the ether component in the system was removed. To the water layer obtained, concentrated hydrochloric acid was added until pH 1 and the separated organic layer was taken and the organic layer obtained was dried with MgSO₄. After this, purification was done by vacuum distillation and 5.9 g of the desired norbornene derivative NB-3 (boiling point 55 ~ 60 deg C / 4 mmHg) was obtained.



By the ¹⁹F-NMR, ¹H-NMR, ¹³C-NMR, and IR analysis, the monomer shown above was identified and confirmed.

Solvent
¹⁹F-NMR (溶媒: CDCl₃): -72.5 (6F, d), -73.0 (6F, d), -101.1 (1F, s), -102.0 (1F, s), -103.9 (1F, d), -104.7 (1F, d), -158.4 (1F, d), -161.1 (1F, d)
MS : 314(M⁺), 295 (M⁺-F), 277, 257, 227, 207, 177, 127, 69(CF₃), 66(C₆H₅), 51(CHF₃)

Example of Application 30 (Synthesis of norbornene derivative (NB-3(1)))

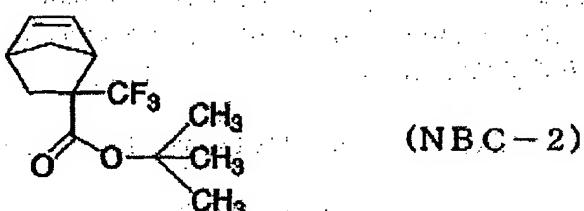
In a 500 ml flask having 4 openings and equipped with a magnetic stirring element, dropping funnel, 3-way cock and thermometer, 10.6 g (0.26 mol) of NaH was placed and the purging with nitrogen was done. Then, 110 ml of THF was added. Under ice-bath cooling, 60 ml of THF solution of 69.1 g (0.22 mol) of norbornene derivative NB-3 was dropped slowly. The dropping was done taking 1 hour and the temperature was returned to the room temperature and then stirring was done for 2 additional hours. After this, cooling was done by the ice bath again and then 26.0 g (0.28 mol) of ethoxy methyl chloride was added slowly from a dropping funnel. After this, at room temperature, stirring was done overnight. The crude product was added to about 500 g of ice water and, while stirring, extraction was done with diethyl ether. By using a separating funnel, the organic layer was separated and the water layer was extracted 2 times with 100 ml of diethyl ether. Organic layers were put together and this was washed with sodium bicarbonate water (Translator's note: the two Chinese characters that were translated here as "sodium bicarbonate water" are actually given in the original text by 3 Chinese characters that would mean "multiple layer water" which does not make sense. These 2 sets of 3 characters have same Japanese pronunciations. If the translation is doubtful, please check with the original writer. The 3 characters in question are on line 3 of p.149 of the original text) and saturated table salt water and the organic layer was dried with $MgSO_4$ and then it was concentrated. Purification was done by vacuum distillation to obtain 55.3 g of the norbornene derivative (NB-3(1)). (Boiling point 62 ~ 67 deg C / 1.5 mmHg).



By the ^{19}F -NMR, 1H -NMR, ^{13}C -NMR, and IR analysis, the monomer shown above was identified and confirmed.

Example of Application 31 (Synthesis of the copolymer of tetra fluoro ethylene / (NB-2) / (NBC-2)

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 24.5 g of the fluorine-containing norbornene derivative (NB-2) that contains OH group (NB-2) which was obtained in Example of Application 4 and 5.8 g of the fluorine-containing norbornene derivative that contains $-COOC(CH_3)_3$ group (NBC-2):



was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After confirming that the liquid temperature reached 40

deg C, the HCFC-141b solution of 6.5 g of (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to occur for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

The unreacted monomer was discharged and next the polymerization solution was taken out and re-precipitation was done with hexane and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 7.8 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-2)/ fluorine- containing norbornene derivative that contains the -COOC(CH₃)₃ group (NBC-2) was 50/ 44/ 6 mol %.

By the GPC analysis, the measured number average molecular weight was 3800.

Example of Application 32 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-2)/ (NBC-2))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 18.3 g of the fluorine- containing norbornene derivative that contains OH group (NB-2) which was obtained in Example of Application 4 and 12.1 g of the fluorine- containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-2) was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.0 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-2)/ fluorine- containing norbornene derivative that contains the -COOC(CH₃)₃ group (NBC-2) was 50/ 38/ 12 mol %.

By the GPC analysis, the measured number average molecular weight was 3200.

Example of Application 33 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-2)/ (NBC-3))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 25 g of the fluorine-containing norbornene derivative that contains OH group (NB-2) and 5.2 g of the fluorine-containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-3) which was obtained in Synthesis Example 3 was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.1 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine-containing norbornene derivative that contains -OH group (NB-2)/ fluorine-containing norbornene derivative that contains the -COOC(CH₃)₃ group (NBC-3) was 50/ 46/ 4 mol %.

By the GPC analysis, the measured number average molecular weight was 2600.

Example of Application 34 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-2)/(NBC-3))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 15.3 g of the fluorine-containing norbornene derivative that contains OH group (NB-2) and 17.3 g of the fluorine-containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-3) which was obtained in Synthesis Example 3 was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.3 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-2)/ fluorine- containing norbornene derivative that contains the -COOC(CH₃)₃ group (NBC-3) was 50/ 36/ 14 mol %.

By the GPC analysis, the measured number average molecular weight was 2600.

Example of Application 35 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-2)/(NB-2 (2))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 27.5 g of the fluorine- containing norbornene derivative that contains OH group (NB-2) and 4.2 g of the protected fluorine- containing norbornene derivative that was obtained in Example of Application 28 (NB-2 (2)) was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.8 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-2)/ protected fluorine- containing norbornene derivative (NB-2 (2)) was 50/ 46/ 4 mol %.

By the GPC analysis, the measured number average molecular weight was 2700.

Example of Application 36 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-2)/(NB-2 (2))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 21.5 g of the fluorine- containing norbornene derivative that contains OH group (NB-2) and 12.4 g of the protected fluorine- containing norbornene derivative (NB-2 (2)) was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of

reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 9.2 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-2)/ protected fluorine- containing norbornene derivative (NB-2 (2)) was 50/ 39/ 1 mol %.

By the GPC analysis, the measured number average molecular weight was 2900.

Example of Application 37 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NB-3 (1))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 31.1 g of the fluorine- containing norbornene derivative that contains OH group (NB-3) which was obtained in Example of Application 29 and 4.1 g of the protected fluorine- containing norbornene derivative (NB-3 (1)) that was obtained in Example of Application 30 was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.8 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-3)/ protected fluorine- containing norbornene derivative (NB-3 (1)) was 50/ 46/ 4 mol %.

By the GPC analysis, the measured number average molecular weight was 2700.

Example of Application 38 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NB-3 (1))

A 500 ml autoclave attached with a stirring apparatus was thoroughly purged with nitrogen and then, by reducing the pressure, 250 ml of the HCFC-141b solution of 20.7 g of the fluorine-containing norbornene derivative that contains OH group (NB-3) which was obtained in Example of Application 29 and 16.4 g of the protected fluorine-containing norbornene derivative (NB-3 (1)) that was obtained in Example of Application 30 was let into the autoclave. Next, 52 g of tetra fluoro ethylene was let into this and then heating and stirring were done. After checking that the liquid temperature reached 40 deg C, HCFC-141b solution of 6.5 g of bis (4- t- butyl cyclo hexyl) peroxy dicarbonate (TCP) was pressed in. After this, at 40 deg C, reaction was let to go for 6 hours. With the progress of reaction, the gauge pressure dropped from 0.89 MPa G (9.0 kgf/ cm² G) before the reaction to 0.87 MPa G (8.8 kgf/ cm² G).

Unreacted monomer was discharged and then the polymerization solution was taken out and re-precipitation with hexane was done and the copolymer was separated. Vacuum drying was conducted until the constant weight was reached and 8.6 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was tetra fluoro ethylene / fluorine- containing norbornene derivative that contains -OH group (NB-3)/ protected fluorine- containing norbornene derivative (NB-3 (1)) was 50/ 32/ 18 mol %.

By the GPC analysis, the measured number average molecular weight was 2900.

Example of Application 39 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3))

In Example of Application 16, in place of the fluorine-containing norbornene that contains OH group (NB-2) which was obtained in Example of Application 4, 40.0 g of the fluorine-containing norbornene that contains OH group (NB-3) which was obtained in Example of Application 29 was used. Other than this, the same procedure as in Example of Application 16 was followed to conduct the reaction and the polymer was separated and purified in the same way to obtain 5.5 g of the copolymer.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE / fluorine- containing norbornene that contains -OH group (NB-3) was 50/ 50 mol %.

By the GPC analysis, the measured number average molecular weight was 3500.

Example of Application 40 (pKa measurement of various norbornene derivative containing OH group)

At first, the method of measuring pKa of the norbornene derivative containing OH group (NB-1) is shown as an example.

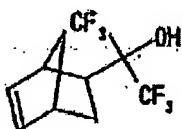
Into the water/ acetone = 10/ 15 ml solution, 0.5846 g of the norbornene derivative containing OH group (NB-1) which was obtained in Example of Application 2 was put in and this was stirred at the room temperature. After checking that the solution was homogeneous, titration was conducted with the NaOH solution of about 0.2 mol/liter. The titration curve was obtained by dropping 0.15 ml of NaOH solution each time and recording the pH at this time. From the inflection point of the titration curve (the point of maximum value of the differential value (Translator's note: "differential value" should be "derivative value"?)) of the titration curve = $d\text{pH}/\text{dml}$, the equivalent point was determined. In this case, the equivalent point was 8.45 ml. The pH that was read off from the titration curve at half value of this, i.e. 4.23 ml, was 11.48. From the titration curve of water/ acetone solution and water solution, the pH difference due to the liquid junction potential difference at the time of 4.23 ml titration was 1.46. So, $11.48 - 1.46 = 10.2$ and the pKa of this norbornene derivative (NB-1) became 10.0.

When 0.7235 g of norbornene (NB-1) was titrated by the same procedure, the equivalent point was 11.2 ml, $\frac{1}{2}$ equivalent point was 5.6 ml and, at the $\frac{1}{2}$ equivalent point, pH became pH = 11.76. At 5.6 ml, the pH difference between the two solutions was 1.38 and, from $11.76 - 1.38 = 10.38$, the pKa of norbornene derivative (NB-1) became 10.4.

When 1.1251 g of norbornene derivative (NB-1) was titrated by the same procedure, the equivalent point was 16.8 ml, $\frac{1}{2}$ equivalent point was 8.4 ml and, at the $\frac{1}{2}$ equivalent point, the pH became pH = 11.37. The pH difference between the two solutions at 8.4 ml was 1.21 and, from $11.37 - 1.21 = 10.16$, the pKa of norbornene derivative (NB-1) became 10.2.

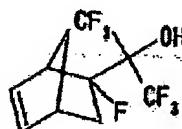
From these 3 trials, pKa of this norbornene derivative (NB-1) was determined to be 10.2.

By using the similar technique, the pKa was measured and determined for the fluorine-containing norbornene derivative that contains OH group (NB-2) which was obtained in Example of Application 4 and the fluorine-containing norbornene derivative that contains OH group (NB-3) which was obtained in Example of Application 29, respectively.



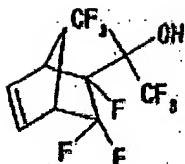
NB - 1

$\text{pK}_a = 10.2$



NB - 2

$\text{pK}_a = 9.0$



NB - 3

pKa = 8.3

Example of Application 41 (Measurement of transparency at the 157 nm wavelength)

Using the fluorine-containing polymers that were obtained in Examples of Application 31 ~ 39, respectively, (1) Preparation of the coating composition, (2) Coating, and (3) Measurement of transparency of the ultraviolet region in vacuum were conducted by the same way as in Example of Application 12. Molecular extinction coefficient at 157 nm is shown in Table 3.

Example of Application 42 (Evaluation of solubility to the development solution)

Using the fluorine-containing polymers that were obtained in Examples of Application 31 ~ 39, respectively, (1) Separation reaction of the protective group, (2) Coating, and (3) Checking of the solubility, were conducted by the same way as in Example of Application 14. Results are shown in Table 3.

Example of Application 43

Using the fluorine-containing polymers that were obtained in Examples of Application 31 ~ 39, respectively, (1) Preparation of the resist composition, (2) Coating, and (3) Measurement of the transparency of ultra violet region in vacuum, were conducted by the same way as in Example of Application 15. Results are shown in Table 3.

Table 3.

Fluorine-contain- ing polymer	Example of Appli- cation 41 Extinction coeffi- cient at 157 nm (μm^{-1})	Example of Application 42 Solubility to the development solu- tion		Example of Appli- cation 43 Extinction coeffi- cient at 157 nm (μm^{-1})
		Before separating protective group	After separating protective group	
EA**31	1.8	Δ*	O	2.0
EA 32	2.3	X	O	2.6
EA 33	1.4	Δ*	O	1.6
EA 34	1.7	X	O	2.0
EA 35	1.8	X	O	2.0
EA 36	2.2	X	O	2.5
EA 37	0.6	O	O	0.8
EA 38	0.7	X	O	0.9
EA 39	0.5	O	-	0.7

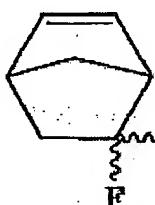
* Δ: Partially dissolving

**EA: Example of Application

Synthesis Example 4 (Synthesis of the norbornene derivative that has -COOH group (NBC-4))

In a 2 liter flask having 4 openings and equipped with a thermometer, stirrer and dropping funnel, 1.2 liters of 1.0 N. - NaOH water solution was added and this was kept below 10 deg C by an ice bath. To this, 158 g of the norbornene compound having -COF group which was obtained in Synthesis Example 1 was dropped slowly. After stirring for 1 hour, 10 % hydrochloric acid water was added to make the pH of the mixture below 2. By chloroform, organic substance was extracted and the chloroform layer was washed with water. After this, drying was done with anhydrous magnesium sulfate.

After the drying, the organic layer was separated and, after removing methylene chloride by distillation, 125 g of the norbornene derivative having -COOH group which is an acid reaction group (NBC-4):



COOH

(N B C - 4)

(melting point 80 ~ 81 deg C/ 0.55 mmHg) was obtained.

For this compound, analyses were conducted by GC-Mass, ¹H-NMR and ¹⁹F-NMR and the structure shown above was identified.

Example of Application 44 (Synthesis of the copolymer of TFE and the fluorine-containing norbornene derivative that contains -COOH group (NBC-4) and the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)))

In Example of Application 18, in place of the fluorine-containing norbornene derivative that contains OH group (NB-2), 1.8 g of the fluorine-containing norbornene derivative that contains -COOH group (NBC-4) which was obtained in Synthesis Example 4, 33.3 g of the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)), 52.5 g of TFE, 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 18 was followed to conduct the polymerization reaction, separation and purification of the polymer to obtain 4.0 g of the polymer.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains -COOH group (NBC-4) / the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)) was 50/ 8/ 42 mol %.

By the GPC analysis, the number average molecular weight was 2800.

Example of Application 45 (Synthesis of the copolymer of TFE and the fluorine-containing norbornene derivative that contains -COOH group (NBC-4) and the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1))

In Example of Application 44, 3.5 g of the fluorine-containing norbornene derivative that contains -COOH group (NBC-4), 29.6 g of the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)) and 52.5 g of TFE were used. Other than these, the same procedure as in Example of Application 44 was followed to conduct the polymerization reaction and the separation and purification of the polymer and 5.0 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains -COOH group (NBC-4) / the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-2(1)) was 50/13/ 37 mol %.

By the GPC analysis, the number average molecular weight was 3000.

Example of Application 46 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NBC – 1)

In Example of Application 37, in place of the fluorine-containing norbornene derivative that contains -OCH₂OC₂H₅ group (NB-3 (1)), 2.3 g of the fluorine-containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-1), 31.1 g of the fluorine-containing norbornene derivative that contains -OH group (NB-3), 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 37 was followed to conduct the polymerization reaction and the separation and purification of the polymer and 4.2 g of the copolymer was obtained.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains -OH group (NB-3) / the fluorine-containing norbornene derivative that contains -COO(CH₃)₃ group (NBC-1) was 50/40/ 10 mol %.

By the GPC analysis, the number average molecular weight was 2800.

Example of Application 47 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NBC – 1)

In Example of Application 46, 2.3 g of the fluorine-containing norbornene derivative that contains -COOC(CH₃)₃ group (NBC-1), 31.1 g of the fluorine-containing norbornene derivative that contains -OH group (NB-3), 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 46 was followed to conduct the polymerization reaction and the separation and purification of the polymer and 5.0 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains –OH group (NB-3) / the fluorine- containing norbornene derivative that contains –COO(CH₃)₃ group (NBC-1) was 50/39/ 11 mol %.

By the GPC analysis, the number average molecular weight was 2500

Example of Application 48 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NBC – 1)

In Example of Application 47, 24.2 g of the fluorine-containing norbornene derivative that contains –OH group (NB-3), 7.0 g of the fluorine- containing norbornene derivative that contains –COOC(CH₃)₃ group (NBC-1), 52.0 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 46 was followed to conduct the polymerization reaction and the separation and purification of the polymer and 4.8 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains –OH group (NB-3) / the fluorine- containing norbornene derivative that contains –COO(CH₃)₃ group (NBC-1) was 50/25/ 25 mol %.

By the GPC analysis, the number average molecular weight was 3200.

Example of Application 49 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-3)/ (NBC – 1)

In Example of Application 46, in place of NBC-1, 9.8 g of the fluorine- containing norbornene derivative that contains –COOC(CH₃)₃ group (NBC-3), 24.2 g of the fluorine-containing norbornene derivative that contains –OH group (NB-3), 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 37 was followed to conduct the polymerization reaction and the separation and purification of the polymer and 4.7 g of the copolymer was obtained.

In the results of analyses by $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains –OH group (NB-3) / the fluorine- containing norbornene derivative that contains –COO(CH₃)₃ group (NBC-3) was 50/37/ 13 mol %.

By the GPC analysis, the number average molecular weight was 2500.

Example of Application 50 (Measurement of the transparency at the 157 nm wavelength)

Using the fluorine- containing polymers that were obtained in Examples of Application 44 ~ 49, respectively, (1) Preparation of the coating composition, (2) Coating and (3)

Measurement of transparency of the ultraviolet region in vacuum, were conducted by the same way as in Example of Application 12. The molecular extinction coefficient at 157 nm is shown in Table 4.

Example of Application 51 (Evaluation of solubility to the development solution)

Using the fluorine-containing polymers that were obtained in Examples of Application 44 ~ 49, respectively, (1) Separation reaction of the protective group, (2) Coating, and (3) Checking of the solubility, were conducted in the same way as in Example of Application 14. Results are shown in Table 4.

Example of Application 52

Using the fluorine-containing polymer (A) that was obtained in Examples of Application 44 ~ 49, (1) Preparation of the resist composition, (2) Coating, and (3) Measurement of transparency of the ultraviolet region in vacuum, were conducted in the same way as in Example of Application 15. Results are shown in Table 4.

Table 4.

Fluorine-contain- ing polymer	Example of Appli- cation 50 Extinction coeffi- cient at 157 nm (μm^{-1})	Example of Application 51 Solubility to the development solu- tion Before separating protective group	After separating protective group	Example of Appli- cation 52 Extinction coeffi- cient at 157 nm (μm^{-1})
EA**44	2	X	O	2.2
EA 45	2.3	Δ*	O	2.6
EA 46	1.2	X	O	1.6
EA 47	0.8	X	O	2
EA 48	2.5	X	O	2.8
EA 49	0.6	X	O	0.8

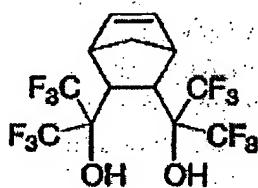
* Δ: Partially dissolving

**EA: Example of Application

Example of Application 53

A 2 liter flask having 4 openings and equipped with a thermometer, stirrer and dropping funnel was dried. After this, 210 g of dimethyl ester derived from 5-norbornene-2,3-dicarboxylic acid anhydride and methanol (THF 100 ml solution) and 900 ml of tetrahydrofuran (HF) were added to the flask having 4 openings and this was dipped in a water bath. To this, 420 g of trimethyl trifluoro methyl silane was dropped, taking 1 hour. At room temperature, this was stirred for 3 hours. After this, the reaction system was cooled with the ice bath again and 50 ml of the 1.0 M tetra hydro furan (THF) solution of tetra butyl ammonium fluoride was added slowly. After stirring for 1 hour, an excess amount of 10 % hydrochloric acid water was added. Organic substance was extracted with methylene chloride and the methylene chloride layer was washed with water. Drying was done with magnesium sulfate anhydride. After the drying, the organic layer was separated and methylene chloride was removed by distillation. After this, by vacuum distillation, 150 g of the reaction intermediate (boiling point 60 ~ 65 deg C/ 2.7 mmHg) was obtained.

Next, in continuation, 143 g of the said reaction intermediate and 400 ml of THF were added to a 1 liter flask having 4 openings and equipped with a thermometer, stirrer and dropping funnel and this was dipped in a water bath at the room temperature. To this, 152 g of trimethyl trifluoro methyl silane was dropped, taking 1 hour. At room temperature, stirring was done for 3 hours. After this, the reaction system was cooled again with the ice bath and 25 ml of the 1.0 M tetra hydro furan (THF) solution of tetra butyl ammonium fluoride was added slowly. After stirring for 1 hour, an excess amount of 10 % hydrochloric acid water was added. By using methylene chloride, organic substance was extracted and the methylene chloride layer was washed with water and next, drying was done with magnesium sulfate anhydride. After the drying, the organic layer was separated and, after methylene chloride was removed by distillation, fractionation was conducted by vacuum distillation and 85 g of the norbornene derivative having $-C(CF_3)_2OH$ group which is an acid reaction group:

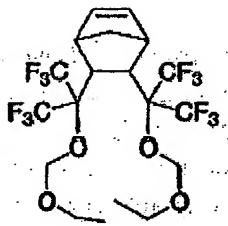


(boiling point 70 ~ 71 deg C/ 1.70 mmHg) was obtained.

For this compound, analyses were conducted by GC-Mass, ¹H-NMR and ¹⁹F-NMR and ¹H-NMR to identify the structure shown above.

Example of Application 54

In a 500 ml flask having 4 openings and equipped with a thermometer, stirrer and dropping funnel, 1.3 g of sodium hydride was placed and drying was done. To this, 150 ml of well-dried tetra hydro furan (THF) was put in and cooling was done with an ice bath. To this, the solution of 22 g of di-funcional norbornene derivative (NB-4) that was obtained in Example of Application 53 and 150 ml of THF was dropped slowly, taking 1 hour. After the dropping was finished, Stirring was done for 3 hours at the room temperature and, after this, the reaction system was cooled again with the ice bath and ethoxy methyl chloride was added slowly. Stirring was done for 1 hour and, further, stirring was done at the room temperature overnight and, after this, an excess amount of 10 % hydrochloric acid water was added. The organic substance was extracted with methylene chloride and the methylene chloride layer was washed with water and, after this, drying was done with anhydrous magnesium sulfate. After the drying, the organic layer was separated and, after removing methylene chloride by distillation, vacuum distillation was conducted to obtain 15 g of the norbornene derivative having $-OCCH_2OCH_2H_5$ group which is an acid reaction group (NB-5):



(boiling point 79 ~ 81 deg C/ 0.50 mmHg).

For this compound, analyses were conducted by GC-Mass, ¹H-NMR and ¹⁹F-NMR and ¹H-NMR to identify the structure shown above.

Example of Application 55 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-4)

In Example of Application 46, in place of the fluorine- containing norbornene derivative that contains OH group (NB-3), 46.9 g of the fluorine- containing norbornene derivative that contains -OH group (NB-4) which was obtained in Example of Application 53, 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 46 was followed to conduct the polymerization reaction and the separation and purification of the polymer to obtain 5.3 g of the copolymer.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains -OH group (NB-4) was 50/50 mol %.

By the GPC analysis, the number average molecular weight was 2400.

Example of Application 56 (Synthesis of the copolymer of tetra fluoro ethylene/ (NB-5)

In Example of Application 46, in place of the fluorine- containing norbornene derivative that contains OH group (NB-3), 59.6 g of the fluorine- containing norbornene derivative that contains -OH group (NB-5) which was obtained in Example of Application 54, 52.5 g of TFE and 6.5 g of TCP were used. Other than these, the same procedure as in Example of Application 46 was followed to conduct the polymerization reaction and the separation and purification of the polymer to obtain 5.3 g of the copolymer.

In the results of analyses by ¹H-NMR and ¹⁹F-NMR, composition ratio of this copolymer was TFE/ the fluorine-containing norbornene derivative that contains -OH group (NB-5) was 50/50 mol %.

By the GPC analysis, the number average molecular weight was 2200.

Use Potential in Industry

The fluorine-containing polymer that is obtained by polymerization using the novel norbornene derivative of this invention as the copolymerizing component has excellent transparency and improved resistance to dry etching and it is useful as the material for use in the chemically amplified photo resist for use with the F₂ laser.